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Purification of Organic Materials and Study of Polymers Therefrom

Final Report
1 July 1965 to 30 June, 1966

Prepared For
Department of the Navy
Naval Air Systems Command
Code 52032

Contract NOW 65-0490-c

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PLASTIC 00262

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Prepared by: R.J. Koshar
W.C. Johnson

Approved by: W.S. Friedlander, Director
Contract Research Laboratory
J.W. Copenhaver, Executive Director
Central Research Laboratories

Central Research Laboratories
MINNESOTA MINING AND MANUFACTURING COMPANY
St. Paul, Minnesota 55119

CC043

FOREWORD

This report summarizes the research carried out by the Minnesota Mining and Manufacturing Company in its Central Research Laboratories during the period 1 July 1965 through 30 June 1966 under Contract NOw 65-0490-c.

The work reported was performed by W. C. Johnson and R. J. Koshar with characterization and analytical support by C. D. Green, D. F. Hagen, M. R. Hallwachs, J. J. McKeown, R. M. Screatton, J. W. Todd and R. J. Wann.

TASK

The Contractor shall conduct an investigation to attain and measure the high degree of purity of organic materials to improve the performance and uniformity of polymeric materials.

ABSTRACT

The attainment of the high degree of purity of monomers was investigated to improve the performance of two selected polymers. [Major emphasis was on the purification of adipic acid and hexamethylenediamine and the study of the effects of high monomer purity on the properties of nylon 66. The properties of a standard grade nylon prepared from high quality commercial adipic acid and distilled hexamethylenediamine were compared with a nylon obtained from monomers purified by repeated crystallization.] The relative purity of the monomers, which were obtained in higher purity by the crystallization processes, was determined by chromatography and freezing point depression studies.² The purity difference between the monomer grades was generally less than 0.1 mole percent. The properties of the two polymer grades were initially compared by viscosity measurements, pyrolysis-chromatographic studies and differential thermal analysis. [Films were fabricated from each polymer grade and their properties compared primarily by electrical measurements and by mechanical property measurements before and after weathering. Nylon 66 obtained from the higher purity monomers was indicated to exhibit a slightly higher molecular weight and a higher tensile strength of films after weathering than the standard grade polymer. No significant improvement of the properties of the higher purity grade nylon was evident by the various other measurements.] Research was also initiated on the purification of monomers and solvents for polymerization to poly[ethylene methylene bis(4-phenylcarbamate)].

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
DISCUSSION	2
A. Purity Considerations	2
B. Poly(hexamethylenedipamide)	4
1. Purification and Analyses of Monomers	4
2. Nylon 66 Salt	6
3. Comparison of the Properties of Nylon 66	8
C. Poly[ethylene methylene bis(4-phenylcarbamate)]	14
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	15
EXPERIMENTAL	16
REFERENCES	34

INTRODUCTION

The degradation of many polymers under service conditions, e.g., exposure to heat, ultraviolet radiation and oxygen, is well known. Although a considerable amount of work has been reported on the mechanism of the degradation of certain polymers and the effects of additives on retarding the degradation process, little information has been published on the effects of ultra-high purity of monomers on the performance of polymers.

The objectives of this research are to attain and measure the high degree of purity of specific monomers and to determine the effects of their high purity on the performance of the resultant polymer. Attempts were made to establish the ultimate performance that could be expected from selected polymers as well as the extent of effort required for purification of monomers beyond presently used procedures.

The major portion of this research relates to poly(hexamethylenedipamide), nylon 66, and the effects of the high purity of adipic acid and hexamethylenediamine on various properties of the polyamide. Research was also initiated on the purification and measurement of purity of monomers and solvents for polymerization to poly[ethylene methylene bis(4-phenylcarbamate)].

DISCUSSION

A. PURITY CONSIDERATIONS

The nature of the extraneous material present in monomers and polymers is known to have varying effects on the performance of polymers. In the case of additives which function as stabilizers, e. g., antioxidants and ultraviolet absorbants, the effect is generally beneficial and results in prolonging the service life of the polymer. Materials, which can be truly regarded as contaminants, are those which cause undesirable effects such as premature termination, crosslinking, cyclization and cleavage of polymer chains during the polymerization process.

Contaminants inadvertently introduced into highly purified monomers and polymers can also have an appreciable effect on the performance of the polymers in that they may effect autocatalytic polymer degradation. As the absolute purity of the monomer is approached, the probability of contamination by ambient media becomes appreciably greater, especially for highly reactive monomers. Impurities present in polymerization solvents or other media can introduce extraneous material into the polymer which could have a greater effect on the properties of the polymer than trace contaminants originally present in monomers. In the case of polyamides prepared by melt polymerization, any inadvertent ingress of oxygen during polymerization results in oxidation of the polyamide chain, i. e., by peroxide formation, accompanied by gel formation and discoloration.

The purity of discrete compounds, such as monomers, is to be differentiated from that of the "purity" of polymers which are inherently composed of mixtures having the same repeating units and end groups but varying molecular weights. It is probable that polymers obtained from the highest purity monomers, i. e., absolute purity, could exhibit at least some degree of chemical inhomogeneity due to oxidation, hydrolysis or other reactions occurring during the preparation, isolation or processing of the polymer.

During the course of this investigation, efforts were made to maintain consistency throughout all phases of the polymerization, handling of monomers and polymers and the fabrication of films in order to obtain a correlation of the high degree of monomer purity with the properties of the resultant polymer.

B. POLY(HEXAMETHYLENEADIPAMIDE)

In efforts to obtain valid conclusions concerning the effects of the high purity of monomers on the properties of nylon 66, a standard grade nylon 66 was initially prepared as a reference. The standard grade polymer was synthesized by melt polymerization of the balanced salt of a high quality commercial adipic acid and a distilled sample of hexamethylenediamine. Various properties of the standard grade polymer were then compared with the properties of nylon 66, designated as the higher purity grade, which was synthesized under similar conditions from higher purity grades of adipic acid and hexamethylenediamine. Viscosity measurements, differential thermal analyses, pyrolysis-chromatographic studies as well as mechanical and electrical property measurements on films were used in attempts to correlate the degree of monomer purity with the performance of the polymers.

The commercial adipic acid and the hexamethylenediamine used for polymerization to the standard grade nylon 66 exhibited high purity to the extent of greater than 99.6 mole percent. The relative difference of the purity of the monomers used for preparing the standard grade polymer and the higher purity monomers used in this study was indicated to be less than 0.1 mole percent.

1. Purification and Analyses of Monomers.—Various methods were investigated for the purification and measurement of purity of hexamethylenediamine. During all phases of this work, the avoidance of contact of the diamine with air was essential to prevent contamination, e. g., reaction with carbon dioxide¹. Purification of hexamethylenediamine was accomplished by fractionation, under reduced pressure, of a commercial product (containing 10% water) followed by repeated recrystallization of one of the distillates from hexane. The crystallization process was repeated five times under nitrogen in a closed crystallization unit. The recrystallized amine was used for polymerization to the higher purity grade nylon. One of the distillates from the fractionation was selected for polymerization to the standard grade nylon.

The determination of the degree of purity of the distilled and recrystallized grades of hexamethylenediamine was initially attempted by gas-liquid chromatography, employing a sensitive hydrogen flame ionization detector. Four different chromatographic column packings were evaluated in efforts to resolve trace impurities. Considerable attention was given to differentiating between impurities actually

present in the samples and those caused by contamination of analytical samples by inadvertent exposure to air, reaction with solvent impurities or thermal degradation during the analyses. The chromatographic studies revealed essentially no differentiation between the two grades of hexamethylenediamine and realistic trace impurities present in the samples were not detected. One spurious peak (0.05% for each grade) apparently results by thermal decomposition of hexamethylenediamine during the analysis.

Freezing point depression measurements indicate that the recrystallized grade of hexamethylenediamine is 0.03 mole percent higher purity than the distilled grade used for polymerization to the standard grade nylon and 0.21 mole percent higher purity than a commercial sample which was arbitrarily selected as reference for the measurements. Freezing point depression measurements were also carried out on several distillates obtained by fractionation of the commercial hexamethylenediamine. The results indicate that a substantial refinement of commercial hexamethylenediamine is achieved by efficient fractionation procedures. The middle portion of the distillate contained the higher purity amine.

Commercial grade adipic acid, which was used for the synthesis of the standard grade nylon, was purified by repeated crystallizations from water. Two grades of the recrystallized acid were prepared to determine the effectiveness of the process. One of the grades was obtained by crystallizing twice and another grade was obtained by repeating the crystallization seven times. The determination of the purity of the commercial and the two recrystallized grades of adipic acid was examined by gas-liquid chromatography, freezing point depression studies and chemical analysis. A thermal conductivity detector and the more sensitive hydrogen flame ionization detector, which does not detect water, were used for the chromatographic studies.

Initially, the commercial and the two recrystallized grades of adipic acid were analyzed directly by chromatography, but trace impurities were not adequately resolved. The methyl esters were then prepared from the acids and analyzed using the flame ionization detector. Seven different column packings were evaluated. Four impurities, which exhibited the same retention time for all of the samples, were detected by analysis of the methyl esters of the three grades of adipic acid.

Three of these contaminants were 0.01% or less for each grade. The major contaminant was indicated to be 0.04% for the commercial grade, 0.03% for the twice recrystallized grade and 0.01% for the adipic acid obtained by repeated crystallizations.

Chromatographic analysis of the methyl esters prepared from the various grades of adipic acid was also carried out using the less sensitive thermal conductivity detector and indicated no detectable impurities. The analysis of the acid (methyl ester) present in the mother liquor, obtained after the initial crystallization, indicated four impurities which were removed during the purification process. The total amount of the impurities in the isolated acid was indicated to be 0.13% by chromatography.

Freezing point depression measurements were carried out to determine the purity level of the two recrystallized grades of adipic acid, relative to the commercial grade. The commercial grade, the twice recrystallized grade and the acid obtained by repeated crystallizations contained 0.43, 0.54 and 0.63 mole percent water, respectively. Since the water present in these samples would not be expected to influence the purity of the resultant nylon salts, efforts were made to estimate the relative amounts of extraneous material other than water present in the samples. The latter determination was based on freezing point depression measurements and water analysis (Karl Fischer reagent). The results (Table VII in the Experimental) indicate that the twice recrystallized acid used for preparing the higher purity polymer is approximately 0.1 mole percent higher purity than the commercial acid, when only extraneous materials other than water are considered. A slightly higher purity level was indicated for the acid obtained after seven crystallizations. The effectiveness of the crystallization process was also evident by freezing point measurements with the adipic acid recovered from the water phase after the initial crystallization. The measurements indicated that the recovered acid is about 0.2 mole percent lower purity than the commercial grade.

2. Nylon 66 Salt.— During this investigation, the preparation of the balanced salts of adipic acid and hexamethylenediamine was essential since the presence of any excess amine or acid in the salt can affect the polymerization results. The salts were obtained by reacting stoichiometric amounts of the monomers followed by a single crystallization. It is probable that certain nonbasic or nonacidic trace impurities present in the monomers could have been reduced or removed during the preparation of the salts.

A standard grade nylon salt (pH, 7.63) was prepared from the commercial adipic acid and the freshly distilled hexamethylenediamine. A higher purity grade salt (pH, 7.60) was prepared from the twice recrystallized adipic acid and the hexamethylenediamine which was purified by repeated crystallizations from hexane. The properties of the salts were compared by infrared and emission spectroscopy, differential thermal analysis, pyrolysis-chromatographic analysis and chemical analyses.

A distinct differentiation between the standard and higher purity nylon salts was evident when the salts were heated in air. The standard grade salt discolored in air at its melting temperature (193°C.). Under similar conditions, no discoloration was observed with the higher purity salt. This discoloration is apparently due to oxidation since no appreciable discoloration was observed when the standard grade salt was heated to 280°C. under nitrogen during the polymerization process.

Emission spectroscopic analysis also indicated a slight differentiation between the standard and higher purity nylon salts. In each case, contaminants containing Fe, B, Pb, Mg, Si, Al, Sn, Na, Zn, Ca and K were detected. The standard grade salt contained a total of about 50 ppm. of these elements compared to less than 22 ppm. for the higher purity salt. Compositions containing silicon (15 ppm. for the higher purity grade) were the major contaminants. Of possible significance is the reduction of iron content from 5 ppm. for the standard grade to about 1 ppm. for the higher purity grade.

Pyrolysis-chromatographic analysis was also investigated in attempts to differentiate between the standard and higher purity grade nylon salts. The pyrolyses of the salts were studied at various temperatures between 30° to 450°C. and the pyrolyzate at each temperature was analyzed by chromatography using a hydrogen flame ionization detector. With the exception of varying amounts of trace methanol found present in the salts, the chromatograms of the volatiles from the two grades of nylon salt were essentially the same.

Other methods were used for comparison of the standard and higher purity nylon salts. Infrared analysis and differential thermal analysis showed no differentiation between the two grades. Chemical analyses indicated that the standard grade salt

contained 0.2% water and 0.1% alcohol (calcd. as methanol) compared with 0.2% water and 0.2% alcohol for the higher purity grade salt. The effect of the presence of small amounts of water and methanol (solvent for preparing the salts) in the salts used for the polymerization studies is not known. It is believed that the water and methanol content of the salts is greatly reduced by the high vacuum techniques used to precondition the salts prior to actual polymerization.

3. Comparison of the Properties of Nylon 66.—The procedure employed for the synthesis of nylon 66 involved the initial formation of the prepolymer by heating the nylon salt at 220°C. under vacuum followed by melt polymerization of the prepolymer at 280°C. (vapor bath) under nitrogen. All phases of the polymerization required a careful control of conditions, especially the control of temperatures and the nitrogen flow through the melt, to insure a satisfactory duplication of the polymerization. Although interfacial condensation polymerization would be less difficult to control, melt polymerization was expected to provide more knowledge of the effect of monomer purity on the properties of nylon 66.

Nylon 66 was prepared from the previously described standard grade nylon salt and the higher purity grade salt in efforts to relate the properties of the two polymer grades with the degree of monomer purity. The two nylon 66 grades are similarly designated as the standard grade polymer and the higher purity grade polymer. No appreciable gel formation or discoloration (yellowing) of the two polymer grades was evident.

The properties of the standard grade and higher purity grade polymers were initially compared by viscosity measurements, differential thermal analysis and pyrolysis-chromatographic analysis. Films were fabricated from each polymer grade and a commercial nylon. The properties of the films were compared by measurements of the viscosity change after processing and by electrical and mechanical property measurements. Films were also weathered under controlled conditions and their mechanical properties compared.

Viscosity measurements indicated that a satisfactory molecular weight range for film formation and reproducibility of the polymerization process were achieved. The average inherent viscosity (1% in *m*-cresol) of four samples of the standard

grade polymer was 1.41 and the average deviation was 0.03. The viscosity average molecular weight, \bar{M}_v , was approximately 47,000 based on the intrinsic viscosity-viscosity average molecular weight relationship². Viscosity measurements of the higher purity nylon 66 indicated a slightly higher average molecular weight than the standard grade. The average inherent viscosity (1% in *m*-cresol) of three samples was 1.53 ($\bar{M}_v = 52,000$) and the average deviation was 0.02.

Differential thermal analysis of the standard and higher purity grades of nylon 66 revealed no differentiation between the two grades. The thermograms exhibited distinct heat absorption maxima at approximately 253°C. and 260°C. (fusion temperature). A sharp crystallization exotherm at 235°C. was also observed with each polymer grade.

Pyrolysis-chromatographic analysis was also studied in attempts to differentiate between the standard and higher purity grade nylons. The method consists of subjecting nylon samples to incremental temperature increases from 25° to 450°C. under helium and analyzing the pyrolyzate by gas chromatography. Impurities present to a greater degree in the standard grade nylon would be expected to influence the pyrolyzate distribution sufficiently for detection by chromatography. Pyrolysis of the two polymer grades resulted in similar temperature-pyrolyzate profiles when a thermal conductivity chromatographic detector was used; no significant differences were detected. Formation of cyclopentanone, carbon dioxide, water and other products resulted initially at about 320°C. for each polymer grade. At temperatures up to 450°C., the production of cyclopentanone decreased and a complex product distribution resulted. Pyrolysis at 400°C., for example, resulted in nine peaks in the chromatograms for each grade. In contrast, the use of a hydrogen flame ionization detector revealed 28 peaks in the chromatograms when the two nylons were pyrolyzed at 370°C. Comparison of the chromatograms from the two nylon grades, using the more sensitive detector, also indicated the formation of pyrolysis products having identical retention times; extraneous peaks were not detected. Some differences of the amounts of several minor pyrolysis products were detected by comparison of the latter chromatograms. Valid conclusions concerning the relationship of the differences observed in the chromatograms with the purity of the nylons can not be made, however, since the differences detected could have occurred by small changes in the pyrolytic temperature and by differences of surface area of the nylons tested.

Films were fabricated from the standard and higher purity polymers and the commercial nylon, Zytel 101. Controlled conditions for the preparation and storage of the films were required to obtain a valid comparison of film properties, especially those affected by uniformity, crystallinity and moisture content. Films were obtained by melt-pressing of vacuum dried polymers at 525° F. under nitrogen. The more amorphous films, used for electrical and mechanical property measurements were obtained by rapid quenching at -55° C.

The inherent and intrinsic viscosities of films prepared from the standard and the higher purity nylons as well as the commercial polyamide, Zytel 101, were compared to determine the extent of degradation of the polymers during processing. The viscosity data are presented in Table I. The commercial nylon and the standard grade nylon exhibited at most only a slight decrease of molecular weight during the fabrication of the films. In contrast, it appears that the molecular weight of the higher purity nylon decreased significantly. A slight but distinct yellow discoloration of films prepared from the standard and higher purity nylons was also evident. The yellow discoloration, which was not uniformly distributed and was present to the same extent in these films, results by pyrolysis and/or oxidation during the thermal treatment. Films obtained from the lower molecular weight commercial nylon showed no appreciable yellow discoloration. The apparent absence of yellowing is indicative of the importance of stabilizers in the commercial nylon which retard degradation, i. e., oxidation, during the fabrication of films.

The initial mechanical properties of films from the standard and higher purity nylons were also compared. The comparison of the tensile strength, modulus, stress at yield and the elongation of the films is presented in Table II. No significant differences between the properties of the films from the two polymer grades were evident. The similarity of the mechanical properties of the two film grades is clearly shown by the comparison of one of the films (sample No. 3) from the standard grade nylon with a film (sample No. 2) from the higher purity grade nylon.

Films from the standard and higher purity nylon grades were exposed to light and moisture for 200 hours in an Atlas Weather-Ometer and their mechanical properties were again compared. Transparent films, free from noticeable discoloration, were obtained after weathering. Comparison of the tensile strength, modulus,

Table I. Viscosity of Nylon Films After Processing^a

Nylon Grade	Viscosity Before Processing		Viscosity of Films ^b	
	$\langle \eta \rangle$	$[\eta]$	$\langle \eta \rangle$	$[\eta]$
Zytel 101	1.14	1.38	1.10 (0.01)	1.23 (0.01)
Standard	1.39	1.71	1.39 (0.03)	1.74 (0.05)
Higher Purity	1.51	1.91	1.38 (0.02)	1.66 (0.02)

^aThe inherent viscosities, $\langle \eta \rangle$, were measured as 1 percent solutions in *m*-cresol and the intrinsic viscosities, $[\eta]$, were obtained by measuring the inherent viscosities at various concentrations and extrapolating to infinite dilution. Triplicate films were obtained from each grade of nylon. In most cases, each film was measured twice.

^bThe average deviation from the mean is given in parenthesis.

Table II. Initial Mechanical Properties of Nylon 66 Films^a

Property	Standard Grade		Higher Purity Grade	
	Range	Sample No. 3	Range	Sample No. 2
Tensile strength, p.s.i.	6230-6770	6770	6480-6780	6780
Modulus, p.s.i. $\times 10^{-3}$	107-111	107	110-114	110
Elongation at break, %	299-310	310	270-321	321
Elongation at yield, %	12-14	12	13-17	13
Stress at yield, p.s.i.	3410-3630	3630	3660-4150	3660

^aTriplicate film samples were prepared from each grade of nylon and several measurements were made with each film.

stress at yield and elongation at yield is presented in Table III. The properties of one of the films from each grade of nylon are also tabulated for comparison. A significant decrease of the tensile strength of both of the two film grades was evident; the greater decrease of tensile strength of films from the standard grade nylon appears realistic. In contrast, films from Zytel 101, which were prepared and weathered under similar conditions, showed relatively little change of the tensile strength after weathering. Comparison of the modulus, stress at yield and elongation at yield revealed no distinct differentiation between the films from the standard and higher purity grade polymers.

Table III. Mechanical Properties of Nylon 66 Films After Weathering ^a

Property	Standard Grade		Higher Purity Grade	
	Range	Sample No. 3 ^b	Range	Sample No. 2 ^b
Tensile Strength, p.s.i.	4150-4650	4150 (6770)	5290-5920	5920 (6780)
Modulus, p.s.i. x 10 ⁻³	98-101	98 (107)	97-99	99 (110)
Elongation at yield, %	18-20	18 (12)	18-21	18 (13)
Stress at yield, p.s.i.	300-320	300 (310)	316-339	316 (321)

^aFilms were weathered for 200 hours in an Atlas Weather-Ometer. The measurements of the elongation at break were erratic and are not presented. The tensile strength of a film from Zytel 101 was 7,300 p.s.i. after weathering; the initial value was 7,380 p.s.i.

^bThe initial properties of the two films before weathering are given in parentheses.

The electrical properties of films from the two grades of nylon 66 were also measured in efforts to correlate the performance of the polymers with the degree of monomer purity. Frequencies ranging from 10² to 10⁷ Hertz and temperatures

ranging from 25° to 145° C. in increments of 10°-20° C. were employed. The relationships of the dissipation factor ($\tan \delta$) to the frequency at the various temperatures were compared and were found similar for the two polymer grades. Dispersion peaks or inflections which could be ascribed to differences of trace ionic impurities were not evident. Figure I shows the dissipation factor - temperature profile at 10^5 Hertz for films from the two nylon grades. The data represents the average values of three films from each polymer grade.

The slight differences, particularly at the dispersion peak at 100° C., are not regarded significant especially when one considers variances which can occur, for example, as a result of small differences of crystallinity, moisture content and general uniformity of the films. The detection of trace impurities in nylon 66 by electrical measurements does not appear to be feasible primarily because of the high polarity inherent in the polymer.

Less polar polymers, e.g., poly(vinyl chloride) and poly(tetrafluoroethylene), would be expected to be more amenable for detection of purity differences by electrical property measurements.

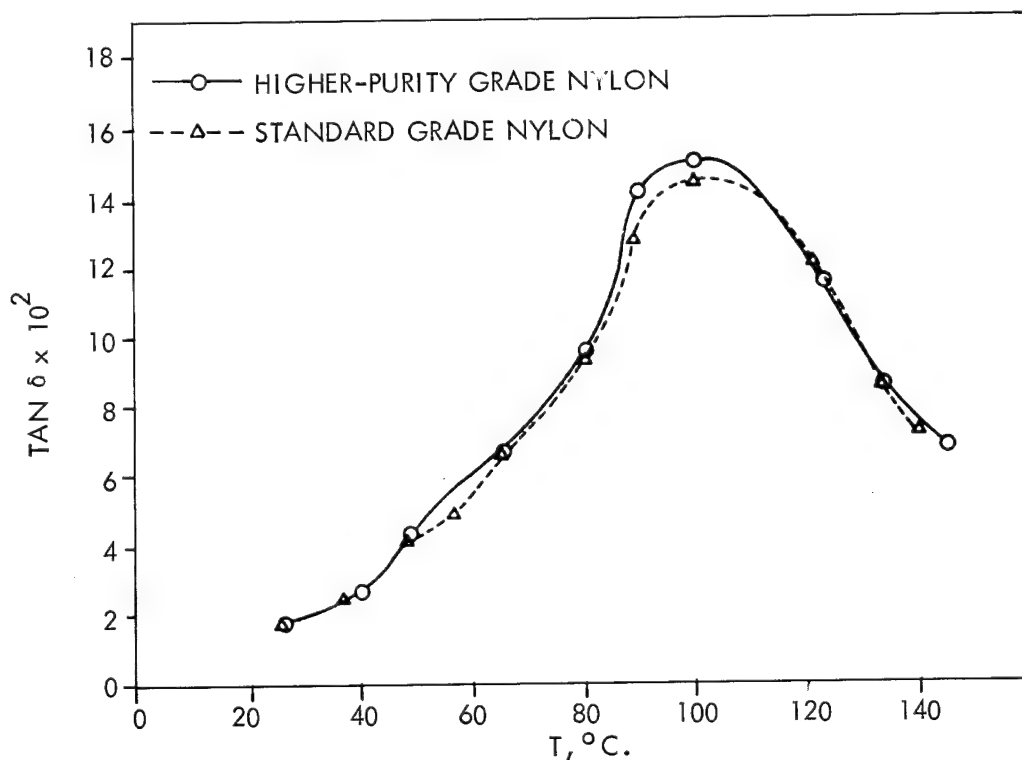


Figure 1. Dissipation Factor Versus Temperature for Nylon Films at 10^5 Hertz

C. POLY[ETHYLENE METHYLENE BIS(4-PHENYLCARBAMATE)]

The purification and measurement of purity of methylene bis(4-phenyl isocyanate), ethylene glycol and solvents used for polymerization to poly[ethylene methylene bis(4-phenylcarbamate)] were initiated. Procedures used for the polymerization of these monomers have been reported.³ Successful polymerization to yield a film-forming polymer requires the reduction of moisture content of each of the monomers and solvents to less than 0.05 mole percent.

Two grades of ethylene glycol were prepared from a commercial grade by a simple distillation to remove water and by fractionation. The initial chromatographic analysis, using a hydrogen flame ionization detector, revealed no appreciable differentiation between the two grades. With each grade the monomer purity, based on chromatography, was indicated to be greater than 99.98%. The water content was 0.01% based on Karl Fischer analyses.

Methylene bis(4-phenyl isocyanate) was prepared from a commercial grade, containing chlorobenzene, by removal of chlorobenzene under reduced pressure followed by a single crystallization from a mixture of reagent grade heptane and hexane. The isocyanate was to be used for conversion to a standard grade polymer. Various chromatographic columns, detectors and procedures were initially investigated to determine the optimum conditions for the detection of trace impurities. The impurities were considered not adequately resolved to enable a valid determination of the degree of purity of the isocyanate. Attempts to improve the analyses by first converting the reactive isocyanate to the less reactive diamine were unsuccessful.

Solvents used for the polymerization were purified and analyzed. Commercial reagent grade methyl isobutyl ketone was fractionated and the purity was indicated to be 99.9% by chromatography. The water content was 0.01%. The purity of a commercial sample of dimethylsulfoxide was indicated to be at least 99.5% by chromatography. The sulfoxide contained 0.01% water and 0.1% acetone as well as additional trace impurities.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The primary objectives of this research were to attain and measure the high degree of purity of adipic acid and hexamethylenediamine and to determine the effects of their high purity on the properties of nylon 66.

The properties of a standard grade nylon prepared from high quality commercial adipic acid and distilled hexamethylenediamine were compared with a nylon obtained from monomers purified by repeated crystallization. The relative purity of the monomers, obtained in higher purity by crystallization, was determined by chromatography and freezing point depression studies; the purity difference was found to be less than 0.1 mole percent.

The properties of the two polymer grades were compared by viscosity measurements, pyrolysis-chromatographic studies and differential thermal analysis. Films were fabricated from each polymer grade and their properties compared by electrical measurements and by mechanical property measurements before and after weathering. Nylon 66, obtained from the higher purity monomers, exhibited a slightly higher molecular weight and a higher tensile strength of films after weathering than the standard grade polymer. No significant improvement of the properties of the higher purity grade nylon was evident by various other measurements.

Additional research on the effects of monomer purity on the properties of nylon 66 should involve: (1) the investigation of methods for attaining a higher degree of monomer purity, approaching absolute purity, (2) the investigation of other analytical methods to establish monomer purity, and (3) a more extensive study to determine significant and realistic differences between polymer grades. The investigation of other polymer systems is recommended.

EXPERIMENTAL

Materials.—Hexamethylenediamine, containing 10% water, was purchased from the R. W. Greeff Company. A sample of hexamethylenediamine, used as a reference for the freezing point depression studies, and ethylene glycol were obtained from the Eastman Kodak Company. Adipic acid (99.6% minimum purity), methylene bis(4-phenyl isocyanate) (solution in chlorobenzene) and Zytel 101 were obtained from E. I. duPont de Nemours and Company. A high purity sample of dimethylsulfoxide was purchased from the Burdick and Jackson Laboratories and the methyl isobutyl ketone (grade 1988) was obtained from the Baker and Adamson Company. All other chemicals used were high quality reagent grade.

Testing and Analytical Procedures.—Measurements of the pH of nylon 66 salts (1% aqueous) were carried out with a Sargent Recording Titrator, Model D, using a Beckman 39142 combination electrode. A duPont Differential Thermal Analyzer, Model 900, was used for the differential thermal analyses of nylon salts and the nylon polymers. Samples of nylon 66 chips were heated under helium at a rate of 20° C./min. A Jarrel-Ash 3.4 Meter Emission Spectrometer was used for trace metal analyses of the nylon salts.

The majority of the chromatographic analyses were carried out on F&M Scientific Corporation Gas Chromatographs, Model 810 and Model 720, using thermal conductivity and hydrogen flame ionization detectors. Helium at 20 to 40 ml./min. was used as the carrier gas. Pyrolysis-chromatographic studies on the adipic acid, nylon salt and nylon 66 were performed by heating samples under helium at controlled temperature increments between 25° to 450° C. The sample was placed in a quartz tube inside a stainless steel loop which could be valve-switched into series flow with the carrier gas stream. A 30-sec. sweep was used at each temperature. The pyrolyzate at each temperature was analyzed by conventional chromatographic methods.

Measurements of the mechanical properties of nylon films were carried out at $72 \pm 2^\circ \text{F.}$ and $50 \pm 2\%$ relative humidity according to ASTM D 882-61T using an Instron testing machine. The crosshead rate was 0.5 cm./min., the gage length was 4 cm. and the strain rate was 12%/min.

The measurements of the electrical properties of the nylon films were carried out at 25° to 140° C. using 10°-20° C. temperature increments and employing frequencies ranging from 10^2 to 10^7 Hertz. A one inch diameter aluminum electrode was vapor coated on each side of the films and the films stored several days at 0-5% relative humidity before testing. Measurements at 10^2 to 10^5 Hertz were made under reduced pressure of less than 50 microns. The samples were preconditioned under vacuum for 15 hours before testing. A General Radio Capacitance Measuring Assembly, 1610-A, was used. Measurements at 10^6 to 10^7 Hertz were carried out in air using a Boonton Q meter, Type 260-A.

Nylon 66 films were weathered in an Atlas Weather-Ometer, Model DMC-H, employing a continuous light source from a twin enclosed violet carbon arc having a spectral range of about 400 to 1400 millimicrons. The temperature range of each cycle (20 min.) was 27 to 60° C. The films were sprayed with water during the final 4 minutes of each cycle.

Freezing point depression studies were performed with a Sargent S-81601 thermometric bridge and a Leeds and Northrup adjustable range recorder. A Sargent S-81620 thermistor was used for studies with hexamethylenediamine and a high range Sargent S-31628 thermistor was used for studies with adipic acid. The sensitivity was 930 and the recorder range was 2.5 millivolts. The freezing point depression constants were obtained by adding known amounts of high purity samples of anthracene and the tetramethyl ester of pyromellitic acid to the reference hexamethylenediamine or adipic acid.

Karl Fischer reagent was used to determine the water content of most of the various chemicals. Methanol was used as solvent for the adipic acid and nylon salts and *m*-cresol was used as solvent for the nylon polymer. The alkyl iodide resulting from the digestion of alcohols with hydroiodic acid was used as a basis for determining the alcohol content of both the nylon salts and nylon polymers. The resulting iodide was distilled into pyridine and titrated potentiometrically using tetrabutyl ammonium hydroxide as titrant.

Handling of Monomers and Solvents.— Although precautions were taken with all of the monomers and solvents to avoid trace contamination after purification, the handling

and storage of the hexamethylenediamine and methylene bis(4-phenyl isocyanate) required special attention. Efforts were made to avoid contact of the monomers and solvents with air. The monomers were stored at 5° C. under nitrogen in sealed, dry amber bottles. The bottles were placed in plastic bags which were filled with nitrogen and contained solid drying agents. The hexamethylenediamine, which was immediately converted to the nylon salt, was handled in a dry box under nitrogen. High purity nitrogen, which was passed through Mallcosorb (Mallinckrodt), Aquasorb (Mallinckrodt) and over copper turnings at 600° C., was used.

Purification and Analyses of Hexamethylenediamine (HMD).—Approximately 40 lbs. of commercial hexamethylenediamine (10% water) was distilled under reduced pressure using a 40 plate Oldershaw column. The major portion (fractions 5 to 20; 78% by weight) of the distillate boiled at 83° C./10 mm. One of the fractions (fraction 15; 790 g.) was selected for the preparation of the standard grade nylon salt.

Purification of 767 g. of the distilled hexamethylenediamine (fraction 14) was accomplished by repeated crystallizations (five times) from 2.5 l. of reagent grade hexane. To avoid contact of the amine with air, the crystallizations were carried out under nitrogen in a closed, two stage crystallization unit which allowed the repeated crystallizations without removal of the amine or hexane until the final crystallization was completed. Freshly distilled hexane was used for each crystallization. The amine was heated under vacuum to remove hexane. Approximately 660 g. of crystallized hexamethylenediamine was prepared by this process. The hexane solution, containing various extracted impurities, was discolored.

The distilled (fraction 15) and crystallized hexamethylenediamine samples were analyzed by gas-liquid chromatography using a hydrogen flame ionization detector. The following four column packings were evaluated: (1) 5% Amine 220 on Fluoropak 80; the column was heated at 90° to 180° C. at 10°/min., (2) 20% Carbowax 20M and 5% potassium hydroxide on Anakrom P; the column was heated at 100° to 250° C. at 10° C./min., (3) 10% of the silicon XE-60 on Fluoropak 80; the column was heated at 100° to 225° C. at 10° C./min., and (4) 10% Apiezon N on Chromasorb G; the column was heated at 150° to 300° C. at a rate of 10° C./min., the injection port was at 275° C. and the detector at 300° C. The columns were 6 ft. x 0.25 in. Solutions of the HMD in reagent grade chloroform or methanol were injected. The Apiezon N column was the most effective of the columns studied. The initial analyses (CHCl_3

solutions) indicated three identical impurity peaks for each sample. Two of these impurities which eluted after the HMD peak proved to be spurious and resulted by the inadvertent exposure of analytical samples to air during storage. A peak which eluted prior to the HMD peak and amounted to 0.05% by area for each sample also appears to be spurious and apparently results by thermal decomposition of HMD during the analysis. This latter peak was also observed when a sample of HMD was trapped during the analysis and reinjected into the column. Trace impurities were not resolved when HMD samples in methanol were analyzed.

Table IV summarizes the results of the freezing point determinations of the various distilled hexamethylenediamine samples and the recrystallized HMD. The determinations were carried out under nitrogen. The values, reported as mole percent relative purity, are relative to an Eastman grade HMD, which was arbitrarily selected as the reference. Freezing point constants were determined by the addition of known amounts of highly purified anthracene and the tetramethyl ester of pyromellitic acid to the Eastman grade HMD. The constant (scale div./mole percent) was 11.28 based on the average values obtained with the two additives. The data given in Table IV indicate that the recrystallized HMD used for the preparation of the higher purity grade nylon is 0.03 mole percent higher purity than the distilled HMD (fraction 15) used for the preparation of the standard grade nylon and 0.21 mole percent higher purity than the Eastman grade HMD. The results also indicate a significant refinement of HMD during the distillation process. During the freezing point depression studies, the distilled samples of HMD were found to discolor under nitrogen after repeated melting. Under similar conditions, little discoloration was observed with the recrystallized HMD.

Table IV. Comparison of HMD Grades by Freezing Point Depression

HMD Sample	Fraction	Distillate		Relative Purity, ^b Mole, %
		Wt.,g.	Total ^a %	
Distilled Samples	5	150	1	+ 0.007
	8	92	37	+ 0.151
	10	845	49	+ 0.221
	11	104	50	+ 0.205
	15	790	78	+ 0.174
	19	625	99	+ 0.153
Recrystallized				+ 0.207

^aCumulative total by wt. percent of the distillate boiling at 83° C./10 mm. (fractions 5 through 20).

^bThe values are relative to an Eastman grade HMD as reference. The higher values represent a higher purity level.

Purification and Analyses of Adipic Acid.—Commercial adipic acid supplied by duPont (purity specification: 99.6% min.) was used for the preparation of the standard grade nylon. The commercial acid was further purified by recrystallization from water after heating the saturated solution at 80°-90° C. The crystallization process was repeated twice and the crystals were dried at 100° C. under vacuum. About 3000 g. of this grade of acid was obtained and used for polymerization to the higher purity grade nylon. Later in the program, the above twice crystallized acid (875 g.) was recrystallized five additional times from water (deionized and distilled twice) to yield 340 g. of vacuum dried acid. The commercial and the two recrystallized grades of adipic acid were analyzed by chromatography, chemical analysis and by freezing point depression studies.

The three grades of adipic acid were analyzed by gas-liquid chromatography using a hydrogen flame ionization detector. The samples were analyzed as the free acid as well as the methyl and ethyl ester derivatives on a series of columns. The column packings were: (1) 15% silicon XE-60 on Anakrom ABS, (2) 3% silicon SE-52 on Chromasorb G PMCS, (3) 3% silicon XE-60 on Neutraport S, (4) 10% poly(ethyleneglycoladipate) and 2% H_3PO_4 on Anakrom ABS, (5) 10% polyester LAC 446 and 2% H_3PO_4 on Anakrom ABS, (6) 10% FFAP (Wilkins Inst. Co.) on Anakrom ABS, and (7) 10% Carbowax 20M (terephthalic acid terminated) on Anakrom ABS. The percentages are by weight. The column lengths ranged from 4 to 12 ft. and the diameters of the columns were 0.13 or 0.25 in. Each of the columns were evaluated by programming column temperatures from 100° C. to the maximum temperature, which varied from 250° to 290° C. The injection temperature was 290° C. and helium carrier gas flow ranged from 20 to 40 ml./min.

The methyl and ethyl derivatives were prepared by refluxing approximately 100 mg. of the acid with 5 ml. of BF_3 -alcohol reagent, destroying the BF_3 with water and extracting the ester with chloroform. The chloroform solutions were analyzed. The majority of the analyses was carried out with the methyl esters. The use of a fresh, high quality BF_3 -methanol reagent was found essential in these studies. Four impurities were detected in the methyl esters prepared from the three grades of adipic acid using the 4 ft. x 0.13 in. LAC 446 polyester column. The results are given in Table V. The free acids were also analyzed directly, such as by using columns containing silicone rubber, but impurities were not resolved.

Table V. Impurities in Adipic Acid (Methyl Ester)

Component ^a	Peak Area, % ^b		
	Commercial	Recrystallized (2)	Recrystallized (7)
1	0.04	0.03	0.01
2	<0.01	<0.01	<0.01
3	0.01	0.01	0.01
4	<0.01	<0.01	<0.01
5 (dimethyl adipate)			

^aThe components are given in order of elution.

^bThe number of crystallizations is given in parentheses.

The adipic acid recovered from the mother liquor, resulting after two crystallizations, was converted to the methyl ester by the previously described procedure. The dimethyl adipate sample in benzene was analyzed by chromatography employing an 18 ft. x 0.25 in. column composed of 3% by wt. of Carbowax 20M on Haloport. The column temperature was at 200°C. and a thermal conductivity detector was used. Four impurities were detected in the sample. The order of elution of the components and area % are as follows: 1(0.02%), 2(0.05%), 3(dimethyl adipate), 4(0.01%) and 5(0.04%). Chromatographic analysis under similar conditions of the methyl esters prepared from the commercial acid and the recrystallized grades of adipic acid failed to reveal the above impurities, indicating that the concentration of these impurities was below the level of detectability of the thermal conductivity detector.

The water content of the various grades of adipic acid was determined by using a Beckman Aquameter and Karl Fischer reagent; methanol was used as the solvent. Although small amounts of water do not interfere with the preparation of the nylon

salts, the accurate determination of the water content was necessary for determining purity differences due to extraneous material other than water by freezing point depression studies. The average water content, based on several determinations on each grade of acid, is presented in Table VI. Analysis was carried out on the commercial grade, the two recrystallized grades and the acid recovered from the mother liquor obtained after the initial crystallization. The standard deviation was estimated to be 0.021 mole percent and the 95% confidence level of all determinations was ± 0.041 mole percent.

Table VI. Determination of Water in Adipic Acid^a

Adipic Acid ^b	H ₂ O, Wt. %	H ₂ O, Mole %	Determinations
Commercial	0.053	0.433	5
Recrystallized (2)	0.066	0.539	5
Recrystallized (7)	0.077	0.625	3
Acid from Mother Liquor (1)	0.061	0.494	2

^aThe average water content based on several determinations is given.

^bThe number of crystallizations is given in parentheses.

The freezing point depression determinations were carried out with the same apparatus used for hexamethylenediamine except that a high range thermistor (Sargent No. S-31628) was employed. The acid was melted directly into a glass tube and the tube placed in a constant temperature apparatus, set at 135°C. The freezing point constant (6.467 scale div./mole %) was determined by adding known amounts of anthracene and the tetramethyl ester of pyromellitic acid to the commercial adipic acid. The average values for the two additives were 6.346 and 6.588, respectively. The purity levels of the two grades of crystallized adipic acid and the acid recovered from the mother liquor after the initial crystallization are presented in Table VII and are relative to the commercial adipic acid. Table VII presents the relative purity of the acid grades (containing water) by the freezing point depression determinations and an estimation of the relative purity based on extraneous

material other than water. In computing the latter results, the difference of water content (average values) between the commercial acid and the crystallized grades was added to the relative purity value determined by freezing point depression. Since the variance of each of the water determinations is the same, the standard deviation of the difference of water content was estimated to be 0.029 mole percent and the 95% confidence level was estimated to be ± 0.057 .

Table VII. Comparison of Adipic Acid Grades by Freezing Point Depression

Adipic Acid ^a	H ₂ O Mole %	H ₂ O, Mole % by Difference	Relative Purity, Mole %	
			Total ^c	H ₂ O Excluded ^d
Commercial	0.433			
Recrystallized (2)	0.539	0.106	+ 0.005	+ 0.111
Recrystallized (7)	0.625	0.192	- 0.053	+ 0.139
From Mother Liquor (1)	0.494	0.061	- 0.277	- 0.216

^a The number of crystallizations is given in parentheses.

^b The mole percent values are relative to the commercial adipic acid. The positive values indicate a higher purity level and the negative values indicate a lower purity level.

^c The total mole percent relative purity was obtained by freezing point depression studies and includes water present.

^d The relative purity due to materials other than water is estimated. The values were obtained by adding the values in column three (mole percent water by difference from commercial acid) to the total relative purity obtained by freezing point depression determinations.

Preparation of Nylon 66 Salts.—Pyrex glassware was cleaned, oven dried and cooled under nitrogen before use. Dry ground glass connections or Teflon adaptors were used to avoid contamination. In a one liter, three-necked flask, fitted with a stirrer, was placed 61.515 g. (0.42 mole) of adipic acid (purified by crystallization twice from water) and 440 ml. of absolute ethanol. The system was heated to 35°C. under nitrogen with stirring to dissolve the acid and the solution then allowed to cool to room temperature. A solution of 48.890 g. (0.42 mole) of the hexamethylenediamine (purified by crystallization from hexane) in 80 ml. of absolute ethanol was charged to an addition funnel under nitrogen in a dry box and the funnel attached

to the flask. The hexamethylenediamine solution was gradually added to the stirred adipic acid solution over a period of two hours. The addition funnel was rinsed with 40 ml. of ethanol, the ethanol solution added to the contents of the flask and the resultant mixture stirred rapidly for one hour. After remaining at room temperature for 15 hours, the salt was filtered, washed with ethanol and dried under vacuum to yield 108 g. of the salt.

The salt was crystallized from a one liter methanol-water solution (90% reagent methanol and 10% distilled water) and the salt dried at 75°C. at less than 1 mm. for 11 hours in a rotary evaporator. The yield of the higher purity grade salt was 76.0 g. Table VIII summarizes some of the properties of this higher purity salt and a standard grade salt prepared under similar conditions from distilled hexamethylenediamine (fraction 15) and commercial adipic acid. The standard grade salt contained 0.2% water and 0.1% alcohol (calcd. as CH_3OH). The higher purity salt contained 0.2% water and 0.2% alcohol as determined by chemical analyses. No differentiation between the samples was evident by infrared analysis.

Table VIII. Properties of Nylon Salts

Property	Standard Grade	Higher Purity Grade
M.p., °C. ^a	192.0-192.5 ^b	192.5-193.0
pH (1% aqueous)	7.63	7.60
Emission Spectroscopy (trace metals, p.p.m.)	Fe (5), B(2), Pb(1) Mg(5), Si(20), Al(4) Sn(3), Na(2), Zn(2) Ca(2), and K(4)	Fe (1), B(1) Pb(1), Mg(2) Si(15), Al(3) Sn(1), Na(1) Zn(2), Ca(2) and K(3)

^aCapillary melting point tubes open to the air were used.

^bThe standard grade salt discolored at 190°C.

Pyrolysis-chromatographic studies were carried out with the standard and higher purity grade nylon salts employing temperatures in increments between 30° to 450° C. Table IX shows the data obtained with the standard grade nylon salt and illustrates the general pattern of volatile evolution at 220° to 450° C. employing the hydrogen flame ionization detector. Peak 6 was identified by elution time as methanol and the majority of it is released from the sample before substantial degradation takes place. Peak 13 was indicated to be cyclopentanone. The increase of peak 6 at high temperatures is most likely to be due to a decomposition product with the same retention time as methanol. The higher purity grade nylon salt gave essentially the same pattern of volatiles with slightly greater amounts of methanol.

Table IX. Volatiles from Standard Grade Nylon Salt by Pyrolysis-Chromatography^a

Peak No.	Pyrolysis Temperature				
	220°	250°	300°	375°	450°
1	3	28	28	160	9090
2	-	110	29	55	2690
3	1	-	23	20	60
4	4	-	6	53	3460
5	-	4	4	13	(b)
6	360	8	1	10	240
7	1	1	1	5	110
8	1	3	7	21	130
9	-	4	4	21	160
10	2	7	8	6	16
11	-	-	-	4	-
12	8	10	6	11	260
13	2	69	244	3200	2460

^aA 6 ft. x 0.25 in. column composed of 5% by wt. of Ethofat on Fluoropak 80 was used. The column was at 90° C. for 7 min., and then heated to 140° C. at 10°/min. The values at the various temperatures are peak heights. A hydrogen flame ionization detector was used.

^bThe peak was lost as a shoulder.

Nylon 66.— A modification of the apparatus and procedures described in the literature was used⁴. The general method is described in detail in the following example. A clean Pyrex glass polymer tube having a 20 cm. x 2.5 cm. standard wall body and a 20 cm. x 1 cm. heavy wall stem was flamed under vacuum and charged under nitrogen with 10.1 g. of the crystallized nylon salt. The tube was alternately evacuated to 40 microns and filled with nitrogen. After three cycles, the tube was evacuated to 30 microns for two hours and then sealed. The ampoule was heated at $220 \pm 2^\circ \text{C}$. (metal tube containing silicon oil) for two hours. The ampoule was then opened under nitrogen and fitted with a clean stainless steel adaptor which was equipped with a 0.3 mm. bore, heavy-walled capillary inlet and a glass side arm to allow the escape of volatile products during the polymerization. Swagelok fittings having Teflon or nylon ferrules were used. The capillary inlet, which was adjustable, was extended into the polymer tube so that the end of the capillary tube was located slightly above the solid prepolymer. The side arm of the adaptor was connected to a trap cooled at -78°C . and the capillary inlet was connected to a high vacuum manifold which contained a storage bulb filled with nitrogen and a nitrogen inlet. The high purity nitrogen source was passed through copper turnings heated to 600°C . to remove oxygen.

The entire system was alternately evacuated to about 40 microns and filled with nitrogen. After three such cycles, the system was opened to an end bubbler attached to the trap and purged with nitrogen for 10 min. After adjusting the flow rate of nitrogen (0.5 ml./min.), the polymer tube was placed in a preheated vacuum-jacketed vapor bath containing dimethyl phthalate (b. p., 279°C .). The heating of the vapor bath was controlled so that reflux in the condenser occurred after 35 min. The prepolymer was heated for an additional 15 min. and the capillary inlet was lowered into the polymer melt. The polymer melt was then heated for an additional 2.3 hours while maintaining a nitrogen flow through the melt. The flow of nitrogen was controlled by employing a constant nitrogen supply at 755 mm.; a Wallace and Tiernan Differential Pressure Gauge was used for the measurement of the pressure. The capillary inlet was then raised from the melt and the heating of the vapor bath discontinued. After 15 min., the polymer tube was removed from the vapor bath and the polymer was allowed to cool under a constant flow of nitrogen.

The outside of the polymer tube was rinsed with acetone to remove the dimethyl phthalate, and then dried. The polymer tube contained a polymer plug and a film above the plug which adhered firmly to the walls of the tube. In order to remove the plug free from glass, the tube was cooled in Dry-Ice, scratched just above the plug and the scratch mark touched with a hot glass rod. The polymer plug (6.5 to 7.0 g.) was crushed in Dry-Ice, dried at room temperature at less than 50 microns for 24 hours and then stored under nitrogen in the dark.

All of the polymerizations were performed under essentially identical conditions using the same time cycle for each operation. The inherent viscosities (1% in *m*-cresol) of four standard grade polymers were 1.38, 1.45, 1.41 and 1.39. The intrinsic viscosities of the latter two polymers were 1.79 and 1.71, respectively. The inherent viscosities (1% in *m*-cresol) of the higher purity grade polymers were 1.51, 1.52 and 1.55 and the intrinsic viscosities were 1.91, 1.93 and 1.98, respectively. Chemical analysis indicated about 0.01% alcohol (calcd. as methanol) in each grade of polymer.

The standard and higher purity grades of nylon 66 were pyrolyzed at various specific temperatures in the range of 30° to 450° C. and the volatile products analyzed by chromatography at each temperature. Thermal conductivity and flame ionization detectors were used. A 6 ft. x 0.25 in. chromatographic column composed of 5% by wt. of Ethofat on Fluoropak 80 was used for the analysis using the thermal conductivity detector. The column was heated at 100° to 140° C. at a rate of 10° C. /min. Table X shows the chromatographic pattern of the volatiles from each polymer grade employing a thermal conductivity detector and a pyrolysis temperature of 400° C. It is to be noted that different sample weights were used. The results indicate no appreciable differentiation between the two polymer grades.

Pyrolysis-chromatographic studies using the more sensitive hydrogen flame ionization detector were carried out employing a 12 ft. x 0.013 in. chromatographic column composed of 10% FFAP on Anakrom ABS. The column was heated at 100° to 250° C. at 10° C. /min. Comparison of the chromatograms obtained by pyrolysis of the standard grade and higher purity grade nylons at 370° C. each revealed 28 peaks having the same retention time for each grade; extraneous peaks were not detected. The order of elution of the components and the peaks heights for the higher purity nylon (43 mg.) are as follows: 1(110), 2(30), 3(25), 4(20), 5(23), 6(25), 7(60),

Table X. Degradation Products from Nylon 66 at 400°C. by Pyrolysis-Chromatography^a

Peak ^b	Retention time min.	Peak Heights	
		Standard Grade (46 mg.)	Higher Purity Grade (51 mg.)
1	0.6	14,600	16,680
2	0.7	3,140	3,390
3	1.0	910	1,010
4	2.8	620	690
5	5.4	14	15
6	6.7	16	20
7	9.8	200	220
8	13.7	6	7
9	15.5	6	5

^aA thermal conductivity detector was used.

^bPeak 7 was cyclopentanone.

8(20), 9(20), 10(20), 11(10), 13(1860; cyclopentanone), 14(20), 15(35), 17(35), 18(20), 19(16), 21(5), 22(35), 23(8), 24(5), 27(60), 28(20). The peaks not given were present in trace amounts. Water and oxides of carbon are not detected with flame ionization. A similar pattern was obtained with the standard grade polymer with some variation of the amounts of several of the components, especially components 1 and 2 which appeared greater for the standard grade. Small variances of temperature and surface area of the polymer may have caused these differences. One of the polymer samples indicated a total weight loss of 1.4% after heating to 350°C.

The thermal decomposition of nylon yields 12 fragments (flame ionization) which appear to have the same retention times as adipic acid which decomposes initially at a lower temperature. The adipic acid decomposed appreciably at 240°C. whereas the nylon 66 polymers were found to be relatively stable under helium up to 300°C.

Volatile products from free adipic acid should therefore be detected between 240° to 300° C. if present in the polymer matrix, but these products were not detected with either polymer grade.

The procedures used to compare the electrical properties of films from the standard grade nylon 66 and the higher purity grade nylon 66 were described previously. Temperatures between 25° and 140°C. and frequencies ranging from 10^2 to 10^7 Hertz were used. A comparison of the dissipation factor ($\tan \delta$) with the specific frequency at the various temperatures revealed no significant differentiation between films prepared from the two polymer grades. Table XI shows the dissipation factors at 10^5 Hertz for three film samples prepared from each grade of polymer. The data shows the average values obtained at each temperature and the variances obtained from the three films from each polymer grade. A very similar variance of the dissipation factor of films from each polymer grade was obtained at other frequencies. A distinct differentiation between the films from the two polymer grades was not observed.

Table XI. Dissipation Factor vs Temperature for Nylon 66 Films at 10^5 Hertz

Standard Grade Nylon $\tan \delta \times 10^2$					Higher Purity Nylon $\tan \delta \times 10^2$				
°C.	A	B	C	Av.	°C.	A	B	C	Av.
26	1.9	1.9	2.0	1.9	26	1.8	1.9	1.9	1.9
36	2.2	2.6	2.4	2.4	40	3.0	2.1	2.9	2.7
48	3.2	4.5	4.5	4.1	48	4.0	4.0	4.6	4.2
56	4.4	5.0	4.9	4.8	56	5.3	4.5	4.6	4.8
64	6.7	6.9	5.9	6.5	65	7.8	6.0	5.9	6.6
80	9.7	8.8	9.5	9.3	80	9.6	8.5	10.4	9.5
89	12.9	14.3	11.1	12.8	90	15.8	13.2	13.2	14.1
100	15.2	14.3	13.8	14.4	100	14.7	15.6	14.8	15.0
121	11.6	13.0	11.6	12.1	122	9.8	12.4	12.5	11.6
133	8.9	8.6	8.9	8.8	133	7.6	9.1	9.5	8.7
140	6.9	7.3	7.1	7.1	144	6.0	6.9	6.3	6.4

Film Preparation.—The nylon 66 samples were vacuum dried (< 50 microns) at 50°C . for 8 hours and then placed between 1.2 mil. aluminum sheets which were previously rinsed with heptane and dried thoroughly. The edges of the aluminum sheets were crimped, the envelope slit at one end and flushed with nitrogen for 10 min. through a hypodermic needle. The envelope was sealed and slit at each end just prior to melt-pressing. The samples were melt-pressed at 525°F . employing an initial contact with the platens for 60 secs. followed by pressing at 15,000 p.s.i. for 30 secs. Films used for electrical and mechanical property measurements were quenched rapidly at -55°C . (slush bath of liquid nitrogen and ethanol) in the aluminum envelope. The exterior of the aluminum envelope was then rinsed with acetone, dried thoroughly and the film removed. The films (3.3 to 4.1 mil.) were stored in a desiccator.

Purification and Analysis of Ethylene Glycol.—The Eastman grade ethylene glycol was distilled to obtain two levels of purity. One of the grades which was to be used for the preparation of the standard grade polymer was obtained by a simple one plate distillation to remove water. Another high purity grade was obtained by careful fractionation using a 70 plate column.

About 4 kg. of the commercial grade was distilled (one plate) at 1 mm. to yield 1940 g. of a middle fraction. The progress of the distillation was followed by chromatography using a 3 ft. x 0.25 in. column at 160°C . which was packed with 10% by weight of Carbowax 20M (terminated with terephthalic acid) on Anakrom ABS; a thermal conductivity detector at 248°C . was used. No impurities were detected in the major fraction. Analysis of the distillation residue revealed a considerable enrichment of impurities which were also present in trace amounts in the commercial sample.

Fractionation of 6 kg. of commercial ethylene glycol was carried out at 1 mm. using a 7 ft. x 1 in. column packed with 0.21 x 0.21 in. Octa-pak. A middle fraction (3900 g.) was collected and analyzed by using the previously described Carbowax column. No impurities were detected by use of the thermal conductivity detector.

The ethylene glycol obtained by a simple distillation and the fractionated grade were analyzed by chromatography using the hydrogen flame ionization detector;

the above described Carbowax column was used. The column was heated at 100° to 250° C. at a rate of 10° C. /min. With both grades only 0.02% impurity was detected. Karl Fischer analyses indicated 0.01% water for each grade.

Purification and Analysis of Methylene Bis(4-phenyl isocyanate).—The preparation of methylene bis(4-phenyl isocyanate) which was to be used for the preparation of the standard grade polymer was obtained as follows: The duPont commercial isocyanate, which contained chlorobenzene as a diluent, was heated at 115° C. under vacuum to remove the chlorobenzene. The isocyanate was extracted with reagent grade heptane under reflux and the heptane solution poured into twice its volume of cold reagent grade hexane. The resultant mixture was then kept at 5° C. for 15 hours, the isocyanate filtered and then dried under vacuum. All of the above operations were carried out under nitrogen. About 2000 g. of methylene bis(4-phenyl isocyanate) were obtained.

Various chromatographic columns and procedures were employed to resolve any trace impurities present in the isocyanate. Columns at 225° to 250° C. containing the silicone fluids, SE-30, SE-52 and XE-60 on Anakrom ABS were initially evaluated. Thermal conductivity and the hydrogen flame ionization detectors were used. Essentially a similar performance was obtained with each of the column systems. The chromatograms showed an early solvent peak (chlorobenzene) and a trace impurity eluting prior to the isocyanate peak. The use of the more sensitive flame ionization detector failed to show the presence of additional impurities.

Attempts to use more functionally active stationary phases to resolve additional impurities were not successful. The isocyanate was either irreversibly held on the column or gave evidence of decomposition. Stationary phases evaluated include FFAP (Wilkens Inst. Co.), Carbowax 20M terephthalate, Apiezon N with KOH and Versamide 900.

Methyl Isobutyl Ketone.—The commercial reagent grade methyl isobutyl ketone was fractionated at 740 mm. using a 7 ft. x 1 in. column packed with 0.21 x 0.21 in. Octa-pak. Chromatographic analysis (flame ionization detector) indicated a purity of greater than 99.9%. The water content was 0.01% by Karl Fischer analysis.

Dimethylsulfoxide.—The high purity commercial dimethylsulfoxide was analyzed by chromatography using the hydrogen flame ionization detector. The analysis indicated 0.1% acetone, 0.01% water and two unidentified impurities (0.2% and 0.1%). The water content could not be analyzed by the Karl Fischer method.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Minnesota Mining & Manufacturing Company 2501 Hudson Road St. Paul, Minnesota 55119		2a. REPORT SECURITY CLASSIFICATION Unclassified - open	
		2b. GROUP distribution	
3. REPORT TITLE PURIFICATION OF ORGANIC MATERIALS AND STUDY OF POLYMERS THEREFROM			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report, 1 July 1965 to 30 June 1966			
5. AUTHOR(S) (Last name, first name, initial) Koshar, Robert J., and Johnson, William C.			
6. REPORT DATE July 1966		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS 4
8a. CONTRACT OR GRANT NO. NOW 65-0490-c		9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES Distribution of this report is unlimited.			
11. SUPPLEMENTARY NOTES None		12. SPONSORING MILITARY ACTIVITY Naval Air Systems Command, Dept. of Navy, Washington, D.C. 20360 Code AIR 52032	
13. ABSTRACT The attainment of the high degree of purity of monomers was investigated to improve the performance of two selected polymers. Major emphasis was on the purification of adipic acid and hexamethylenediamine and the study of the effects of high monomer purity on the properties of nylon 66. The properties of a standard grade nylon prepared from high quality commercial adipic acid and distilled hexamethylenediamine were compared with a nylon obtained from monomers purified by repeated crystallization. The relative purity of the monomers, which were obtained in higher purity by the crystallization processes, was determined by chromatography and freezing point depression studies. The purity difference between the monomer grades was generally less than 0.1 mole %. The properties of the two polymer grades were initially compared by viscosity measurements, pyrolysis-chromatographic studies and differential thermal analysis. Films were fabricated from each polymer grade and their properties compared primarily by electrical measurements and by mechanical property measurements before and after weathering. Nylon 66 obtained from the higher purity monomers was indicated to exhibit a slightly higher molecular weight and a higher tensile strength of films after weathering than the standard grade polymer. No significant improvement of the properties of the higher purity grade nylon was evident by the various other measurements. Research was also initiated on the purification of monomers and solvents for polymerization to poly [ethylene methylene bis(4-phenylcarbamate)].			

DD FORM 1 JAN 64 1473

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